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DYNAMIC MECHANICAL BEHAVIOR OF PHOTO-CROSSLINKABLE NONLINEAR OPTICAL POLYMERS

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ABSTRACT

An easily processable photocrosslinking guest-host system with stable second order nonlinear optical properties using polyvinylcinnamate as a host polymer has been developed[1-2]. Samples were made as free standing films from photo-crosslinkable polyvinylcinnamate and different concentration levels of 3-cinnamoyloxy-4-[4-(N,N'-diethylamino)-2-cinnamoyloxy phenyl azo] nitrobenzene. Photo-crosslinking was carried out by ultraviolet radiation at the major wavelengths viz. 297 and 313 nm subsequent to corona poling. Dynamic mechanical properties of these polymer films were investigated. The changes in the storage and loss moduli, as well as relaxation behavior of the system upon crosslinking and poling are discussed.

INTRODUCTION

A potential nonlinear optical material(NLO) for second order applications must possess a noncentrosymmetric organization with large NLO coefficients[3]. Electrically poled NLO active dyes in polymer matrices is one of the attractive approaches because of the flexibility in processing and molecular design. Guest-host systems[3-4] and systems in which the NLO dyes are covalently bonded into the polymer backbone as pendant groups[5] are examples of this approach. Even though these systems are quite easy to prepare, they suffer from temporal decay of the second order NLO properties because of the thermal relaxation of the electrically induced orientation of the NLO moieties. In order to prevent the relaxation of the noncentrosymmetric alignment induced by poling, thermal crosslinking[6] or photo-crosslinking[1-2], which results in more stable SHG signal have been introduced.

The relaxation behavior of the molecules involved in the systems mentioned above is an important subject of study, because it can lead to a better knowledge of the correlation between molecular motion and the decay of the SHG signal. The relaxation mechanisms of NLO chromophores on the main chain and side chain polymers have been studied by dielectric measurements[7-8]. It is believed that the main chain relaxation of the polymer matrices also contributes to the decay of the SHG signal.

Dynamic mechanical measurement is a good tool to study the relaxation phenomena in polymers[9]. It can also be used to monitor the extent of crosslinking reaction. In this paper, we report the mechanical relaxation of a photo-crosslinkable system[1] polyvinylcinnamate and a NLO active dye, 3-cinnamoyloxy-4-[4-(N,N'-diethylamino)-2-cinnamoyloxy phenyl azo] nitrobenzene (CNNB-R) (Figure 1). The storage, loss moduli and relaxation phenomena affected by photo-crosslinking and corona poling were analyzed.

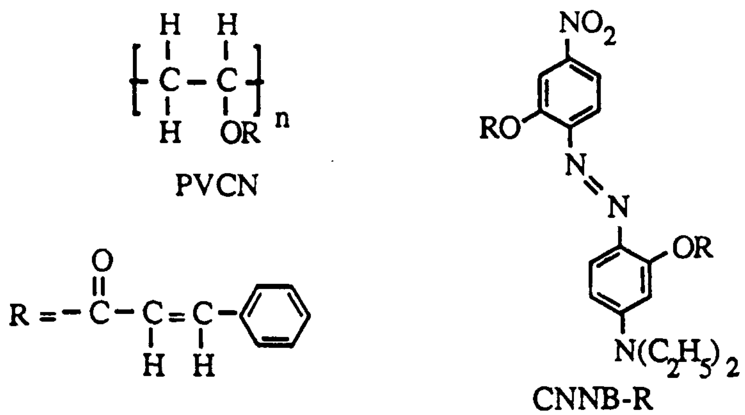

Figure 1 Structures of polyvinylcinnamate(PVCN) and CNNB-R

EXPERIMENTAL

Materials and sample preparation

Polyvinylcinnnate(PVCN) purchased from Polysciences Inc. was used as received. 3-cinnamoyloxy-4-[4-(N,N'-diethylamino)-2-cinnamoyloxy phenylazo) nitro-benzene (CNNB-R) was synthesized in our laboratory[1]. Dichloromethane purchased from Aldrich Co. was dried before use.

PVCN and PVCN with 5% and 10% (by wt) of CNNB-R were dissolved in dichloromethane to a concentration of 1g/15ml. The solutions were then filtered through 10 μm filter paper and 0.2 μm teflon membrane filters in order to remove undissolved impurities. The solutions were then cast onto glass slides placed on a level surface (The slides were framed prior to use, using a protective overlay to keep the solution from flowing out). The solvent was allowed to slowly evaporate. The cast films were dried in a vacuum oven, while gradually increasing the temperature upto 110°C over 48 hr. The films were kept at 110°C for another 12 hr to ensure that all the solvent had been removed. The dried films were then quenched to room temperature. The thickness of films varied from 20 to 30 μm depending on the amount of the solution used. The solvent removal was confirmed by DSC (TA Instrument Co., DSC2910) with a heating rate of 10°C/min. UV-Visible Spectroscopy (Perkin-Elmer, UV/Vis/NIR spectrophotometer Lambda 9) was used to study the extent of thermal crosslinking during the long heating period. The films, while still attached to the glass slide, were cut to a size of 10X20 mm (suitable for the dynamic mechanical measurement) with a hot knife, and then floated off in water. The films were further dried under vacuum at room temperature for an additional 3 hr before the dynamic mechanical measurements.

Photo-crosslinking

Mercury lamp(100W/2, Oriel Co. model 6281) was used for photo-crosslinking experiments. A colored glass filter (UG-11) and a microscope glass slide(thickness, 1.0mm) were used to block the wavelengths above 400nm and below 290nm, respectively. Samples were irradiated on both sides, by exposing each side with a UV intensity of 3-4 mW/cm^2 for different periods of time before the dynamic mechanical measurements.

Corona poling

The corona poling technique using a sharp tungsten needle was performed to align the dipoles in a noncentrosymmetric fashion. The experimental arrangement for corona poling has been discussed elsewhere[10]. Films of 20 µm thickness were placed on the uncoated side of indium-tin oxide(ITO) glass slides. The coated side of the ITO served as the bottom electrode. The corona wire was held at a potential of 9.5KV. The poling temperature was 70-80°C. After poling for 15 min, the samples were cooled down quickly to room temperature. Each side of the sample was then irradiated for 30 min under the same electric field.

Dynamic mechanical measurements

The measurements were performed using a Dynamic Mechanical Analyzer(DMA 983) from TA Instrument Co. The displacement amplitude was 1.00 mm and the oscillation frequency was 1.0 Hz. The ratio of length to thickness was approximately 15. The heating rate was 2.5°C/min. The data obtained were analyzed by DMA Standard Data Analysis software version 4.2.

RESULTS AND DISCUSSION

PVCN is a well-known photo-active polymer which can undergo photo-crosslinking[11], but it is found in our laboratory that it can undergo thermal crosslinking as well. For the dynamic mechanical measurement, the sample must be solvent-free to avoid the plasticizing effect[12] from the residual solvent. However, drying at high temperature may lead to thermally induced crosslinking, which should be minimized. The degree of thermal crosslinking was monitored by UV spectroscopy. The absorbance at 278nm due to the double bonds of the cinnamoyl group was reduced by less than 5% after the drying process. This indicates that the degree of thermal crosslinking that occurred during the process of drying the films was negligible.

Figure 2, 3a, and 3b show the results of dynamic mechanical measurements of the pristine PVCN with and without UV irradiation. As expected[13], UV irradiation caused the crosslinking reaction, leading to an increase in the storage modulus at high temperature, a drastic decrease in the tan δ value and a broadening and shift of the loss modulus peaks to much higher temperatures. The broadening of the loss spectra is due to the variation in the

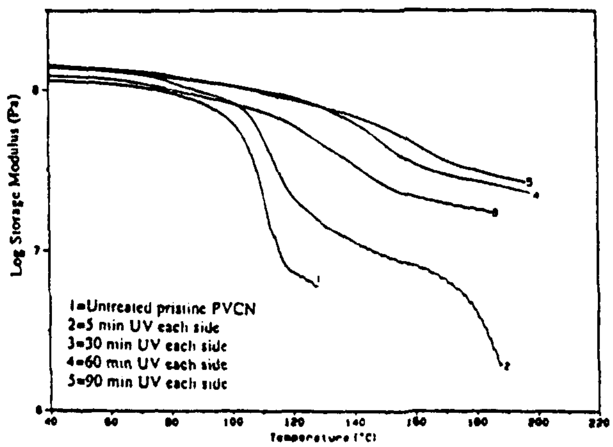

Figure 2 Temperature dependent storage modulus of undoped PVCN subjected to different periods of UV irradiation.

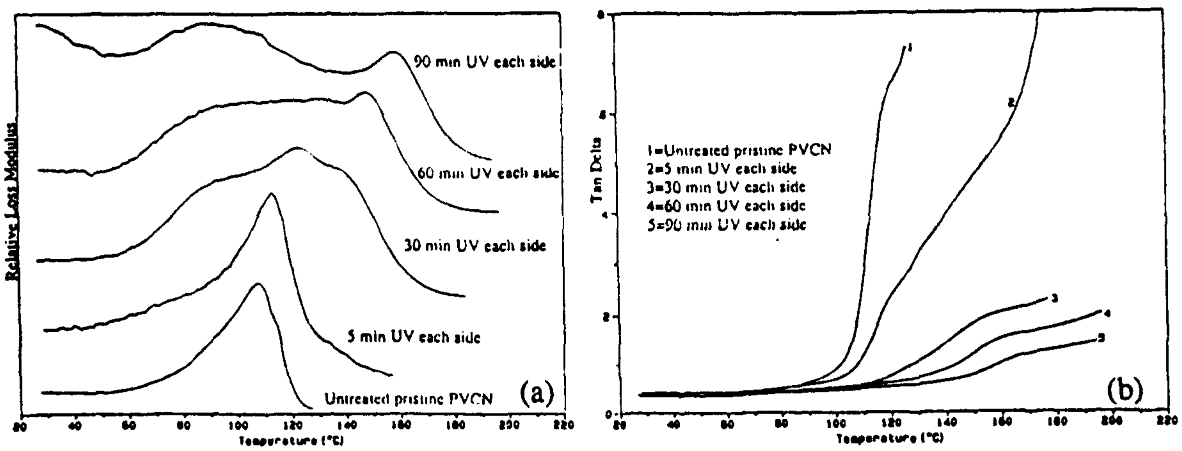

Figure 3 (a) Relative loss modulus; and (b) tan δ vs. temperature for different periods of UV irradiation.

degree of crosslinking within the sample. From figure 3a, the loss modulus spectra of the untreated polymer show some broadening at both higher temperature and lower temperature. At the longest UV irradiation time, the broad loss curve separates into two peaks. The one at the higher temperature corresponds to the movement of the polymer backbone in the network. The other peak at the lower temperature is believed to result from the movement of the uncrosslinked polymer main chain in the middle section of the sample as a result of the skin depth effect.

By adding 5% of NLO dye into the polymer matrix, the loss modulus curve becomes broader. In contrast, increasing the amount of dye to 10% results in narrowing of the loss spectrum, and the broadness at lower temperature disappears as shown in figure 4. It was observed that for a low concentration of plasticizer in a polymer system, the plasticizer could be dispersed in a way that resulted in a gradient of mobility of the polymer backbone[14]. In the case of the sample with 5% dye, the broadening of the loss curve may be a result of the inconsistent segmental mobility caused by the fluctuation of dye concentration, which in turn caused the variation in the relaxation time.

The spectra of storage and loss moduli of 5% and 10% CNNB-R samples before and after the UV irradiation are shown in Figure 5a, 5b, 6a and 6b. After the UV treatment, the storage modulus at the temperature above Tg increased and the E''_{max} temperature shifted toward higher temperature, in a manner similar to the case of the undoped PVCN. This proves

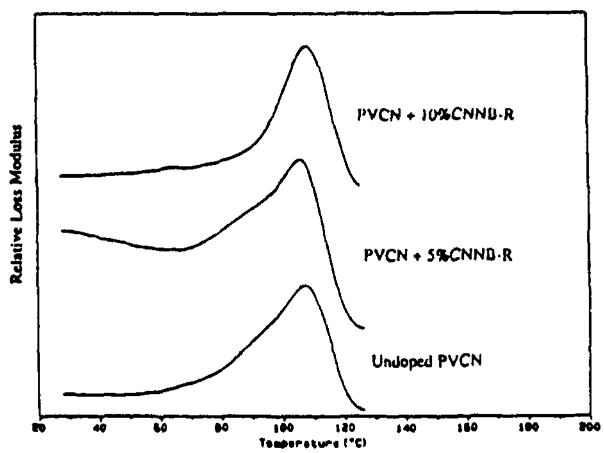

Figure 4 Relative modulus E" as a function of temperature for PVCN with different level of CNNB-R.

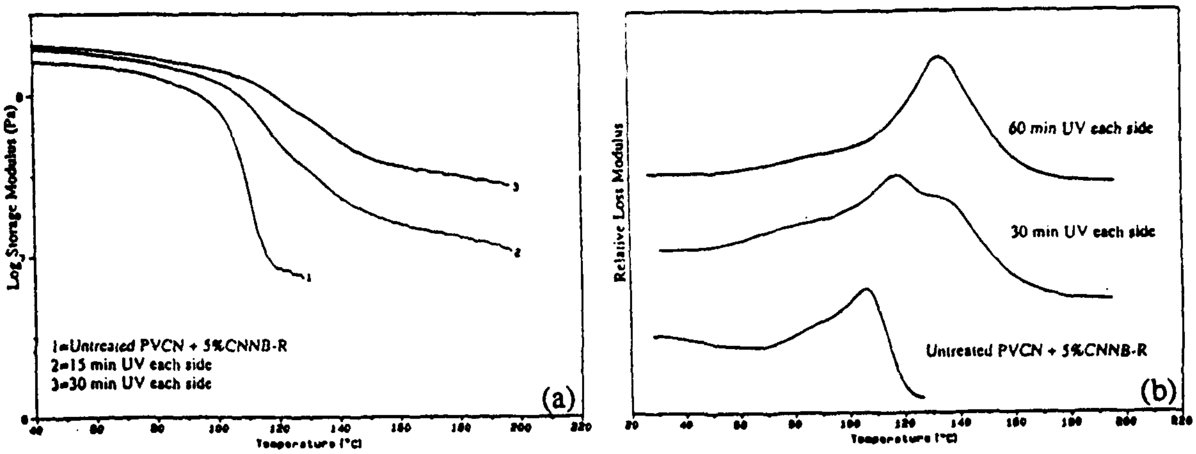

Figure 5 Temperature dependence of (a) storage modulus, and (b) relative loss modulus of PVCN with 5%CNNB-R subjected to different periods of UV irradiation.

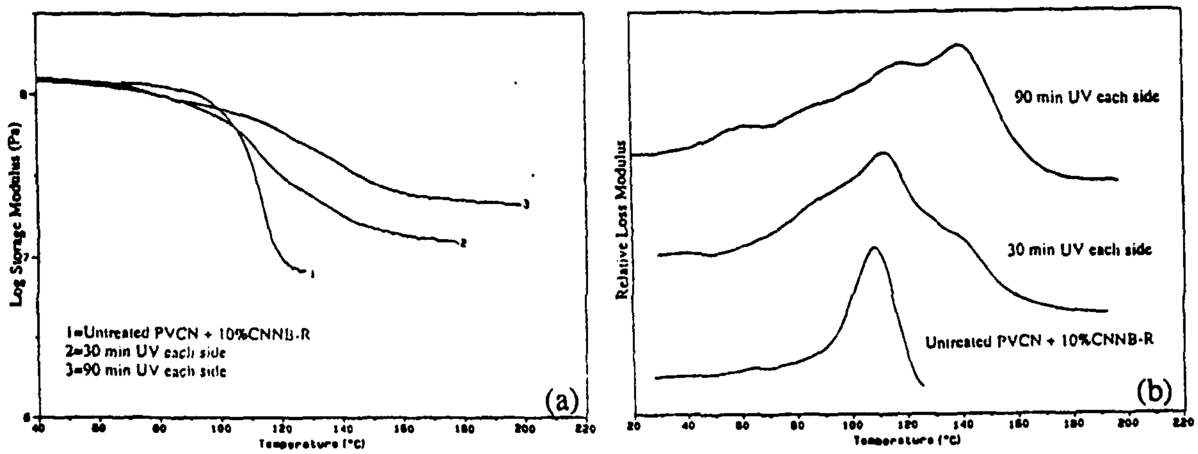

Figure 6 (a) Storage modulus and (b) relative loss modulus vs. temperature for PVCN with 10%CNNB-R subjected to different periods of UV irradiation.

that the network became denser as the irradiation time increased. Figure 7 shows the E" of the sample subjected to UV irradiation under corona field compared to the one without corona poling. It is interesting to observe that the loss peak of the poled sample is narrower than the one without poling. Generally, the broadening of the loss modulus relates to the distribution of

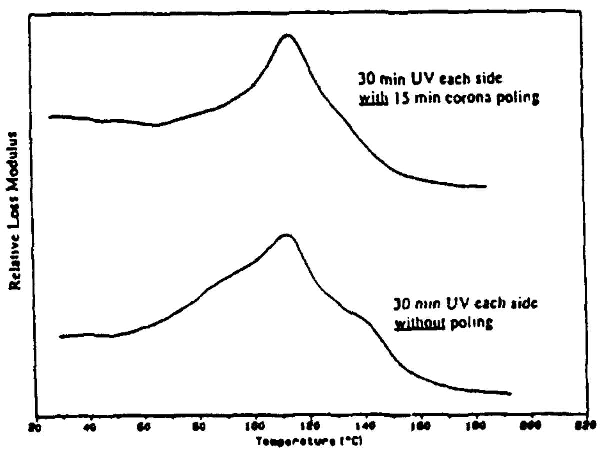

Figure 7 Temperature dependence of loss modulus for PVCN with 10%CNNB-R after 30min UV irradiation on each side; with and without poling.

the molecular weight between crosslinks[13]. As mentioned earlier, corona poling induced a preferential alignment of NLO dye in the polymer matrix. The network may form with a narrower distribution of the molecular weights between crosslinks. In other words, the network was formed in a more homogeneous fashion.

CONCLUSION

These dynamic mechanical studies confirmed that a three dimensional network was formed by the photo-crosslinking reaction. Because of UV treatment, the storage modulus at the temperature above Tg increased. The loss modulus peaks shifted to higher temperatures and the tan δ values decreased. Alignment of the NLO moieties by corona poling technique in this photo-crosslinkable guest-host system resulted in the formation of a more homogeneous network.

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REFERENCES

1. B.K. Mandal, J. Kumar, J.C. Huang, and S.K. Tripathy, Makromol. Chem., Rapid Commun. 12, 63 (1991).
2. B.Mandal, Y.M. Chen, J.Y. Lee, J.Kumar, and S.K. Tripathy, Appl. Phys. Lett. 58, 2459 (1991).
3. K.D. Singer, J.E. Sohn, and S.J. Lalama, Appl. Phys. Lett. 49, 248 (1986).
4. B.K. Mandal, Y.M. Chen, R.J. Jeng, T. Takahashi, J. Huang, J. Kumar, and S.K. Tripathy, Eur. Polym. J. 27, 735 (1991)
5. H.L. Hampsch, J. Yang, G.K. Wong, and J.M. Torkelson, Macromolecules 21, 528 (1988)
6. M.Eich, B.Reck, D.Y.Yoon, C.G. Willson and G. C. Bjorklund, J.Appl. Phys. 66(7), 3241 (1989).
7. I. Teraoka, D.Jungbauer, B. Reck, D.Y. Yoon, R. Twieg, and C.G. Willson, J. Appl. Phys. 69(4), 2568 (1991).
8. D. Jungbauer, I. Teraoka, D.Y. Yoon, B. Reck, J.D. Swalen, R. Twieg, and C.G. Willson, J. Appl. Phys. 69(12), 8011 (1991).
9. T. Murayama, Dynamic Mechanical Analysis of Polymeric Material, (Elsevier Scientific Publisher, Amsterdam, 1978), p.60.
10. M. Eich, A. Sen, H. Looser, G.C. Bjorklund, J.D. Swalen, R. Twieg, and D.Y.Yoon, J. Appl. Phys. 66(6), 2559 (1989).
11. J.A. Brydson, Plastics Materials, 4th ed. (Butterworths Scientific Publisher, London, 1982), pp. 359-360.
12. L.E. Nielson, Mechanical Properties of Polymers and Composites, vol.1, (Marcel Dekker Publisher, New York, 1974), p.189.
13. ____, Ibid., pp. 174-181.
14. D. Lei, J. Runt, A. Safari, and R.E. Newnham, Macromolecules 20,1797 (1987).

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